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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the polymer material which has a nonporous double continuation structure substantially. A nonporous double continuation (bicontinuous) structure is the structure where both of hydrophilic polymer phases and hydrophobic polymer phases are continuing, and each phase moreover shows each bulk properties, substantially. This invention relates also to the manufacturing method of the microemulsion to which a radical polymerization nature monomer exists in both the aqueous phase and an oil phase, and such microemulsion, and the method of reaching and manufacturing a polymer material.

[0002]

[Description of the Prior Art] A surfactant mixture with suitable microemulsion. They are water / oil system colloidal dispersion object stable with [a surface-active agent usually like soap and an auxiliary surface-active agent (cosurfactant) like short chain alcohol]. In contrast with the turbidity emulsion of custom in which stability originates in kinetics purely, microemulsion is thermodynamically stable and is spontaneously formed by contact. It is one with a small (about 10 nm) size of the globular form drop currently distributed in a continuation medium, and is optically transparent.

Encyclopedia of Polymer Science Engineering; Wiley: Please refer to New York 1987 Vol. 9 and p.718.

[0003]Microemulsion differs from a macro emulsion or a mini emulsion. It is an unstable mixture thermodynamically, and one fluid forms the fine drop for which the bigger diameter containing two sorts of immiscible fluids than 100 nm is shown, and is distributing the macro emulsion usually known as an emulsion in the fluid of another side. The macro emulsion has become muddy and is usually carrying out opalescence. A mini emulsion is an opaque thermodynamically unstable emulsion containing two sorts of immiscible fluids prepared using the mixture containing the auxiliary surface-active agent and ionic surfactant like long chain fatty alcohol or n-alkane. In order to prepare a mini emulsion with an average droplet diameter of 100-500 nm, comparatively high mechanical shearing force is required.

[0004]Microemulsion can be an oil-in-water type (water continuation type), a water-in-oil type (oil continuation type), or double continuation type. In double continuation microemulsion, an oil phase and the aqueous phase live together as a continuation domain, and surfactant molecules are located in the interface. The water in a double continuation microemulsion system, an oil, and an auxiliary surface-active agent (usually short chain alcohol) are diffused at the speed which is equal to the speed for Sumishige, respectively.

[0005]The radical polymerization of a vinyl monomer can be attained in either the disperse phase of an oil-in-water type (o/w), a water-in-oil type (w/o), or double continuation microemulsion, or a continuous phase in principle. Kuo and others (Macromolecules, 1987, 20, p.1216) has indicated polymerizing styrene in the disperse phase of o/w type microemulsion. Candau and others (US, 4,681,912, B Description) has indicated polymerizing water soluble monomers in the disperse phase of w/o type microemulsion. Chew and Gan (J. Polym. Sci.: Polym. Chem., 1985, 23, p.2225) tended to polymerize the methyl methacrylate as a continuous phase of a w/o type emulsion which distributed water in the polymer matrix. However, proof that the obtained polymer has taken double continuation structure is not accepted at all. Stoffer and Bone (J. Dispersion Sci. Technol., 1980, 1, p.37). It has reported having

polymerized the methyl methacrylate as a continuous phase in the system which contains sodium dodecyl sulfonate, a pentanol, and water further.

[0006] Shah and others (European patent application No. 391,343) has indicated polymerizing for example, the acrylate system monomer as a disperse phase of aqueous microemulsion, and manufacturing a very small polymer particle. Puig and others (J. Colloid Interface Sci., 1990, Vol. 137, p.308) is discussing the polymerization of the acrylic acid / styrene system microemulsion of a monomer which shows [in / on the other hand (acrylic acid) / the aqueous phase] fusibility remarkably. The obtained copolymer has constituted the gestalt which an acrylic acid unit is dispersed and is distributed at random in a polystyrene block object.

[0007] Above-mentioned document is only teaching the thermal method of making a polymerization starting. There is nothing that has indicated manufacturing the double continuation polymer with which the polymer which has the double continuation structure where both phases are solids or a hydrophobic polymer, and hydrophilic polymer coexist in both phases in these document by the polymerization of microemulsion moreover.

[0008] Price (US, 5,151,217, B Description), It has indicated manufacturing the double continuation microemulsion containing the hydrophobic monomer and cross linking agent like alkyl ester of styrene, acrylate, or methacrylate under existence of a unique addition condensation nature cationic surface active agent. The purpose of Price was to manufacture the solid polymer which can be used for a separation process with photopolymerization method. About using a polar monomer for the method of polymerizing the microemulsion which makes a radical polymerization nature monomer exist in both the aqueous phase and an oil phase, a manufacturing method, or one of phases, it is unstated in any way. Finally, output polymer is not two solid phases and shows one solid phase and one liquid phase.

[0009] There is a report by Cheung and others about photopolymerization of double continuation microemulsion (Langmuir, 1991, Vol. 7, pp. 1378ff., and 2586ff.). Porosity polystyrene membrane is obtained from the microemulsion of styrene/drainage system. It polymerizes in the case where

methyl methacrylate / acrylic acid series microemulsion is not considered as the case where a surface-active agent is made to exist, and it is supposed that the porous polymer solid which has good mechanical stability in both cases was obtained.

According to the report, although the polar monomer is used by these systems, the obtained copolymerization material shows the single phase porosity system by the microscopic inspection.

[0010]European patent publication of unexamined application 0th transferred to the grantee of this invention 432 According to the No. 517 gazette, forming a porous film, film, or bead is indicated by carrying out photopolymerization of the canal phase of the double continuation microemulsion which contains an activity substance further biologically. However, about the polymerization of the monomer in a hydrophilic phase, neither a description nor claim for patent is carried out at all.

[0011]The US, 5,238,992, B Description (Outubuddin) has indicated the composite material and microemulsion polymer blend which were manufactured from the microemulsion containing both a hydrophilic phase and a canal phase and which controlled porosity. This microemulsion contains a surfactant system, an arbitrary auxiliary solvent, and a hydrophilic monomer in a hydrophilic phase, and is prepared as a thing which contains a hydrophobic monomer in a canal phase. As for the obtained blend, even if a stoma is shown in both a micron field and a submicron region and being compared with any of an oil-in-water type or a water-in-oil type, when microemulsion is double continuation type, it is common that porosity becomes high.

[0012]

[Problem(s) to be Solved by the Invention] In the technical field concerned, neither the polymer which has a nonporous double continuation structure substantially also being manufactured, nor the needs for such polymer are recognized. These polymer that has a nonporous double continuation structure substantially, The hydrophilic polarity kind of the radical polymerization nature contained in the aqueous (water) phase of microemulsion and the hydrophobic monomer of the radical polymerization nature contained in an organic (oil) phase are polymerized simultaneously, and it is obtained by forming the polymer which has two sorts of solids which have a nonporous double continuous phase substantially.

[0013]Such polymer that has a nonporous double continuation structure substantially has the useful bulk properties of both hydrophilic polymer and a hydrophobic polymer for especially the use searched for. For example, to moisture and/or bacteria, while it is impermeableness, a breathable film with the high transportability of a steam is desired dramatically. In such polymer, either a hydrophobic substance or a hydrophilic substance can be caught or released gradually. The material in which another bulk properties of one side of a phase or both have an advantage demonstrated simultaneously can also be manufactured. For example, the adhesive acrylate type adhesives made into conductivity can be manufactured by making a hydrophilic phase contain an electrolyte.

[0014]This invention provides the formation method of the microemulsion in which a solid contains both the manufacturing method of a nonporous double continuation polymer material and such a material, and a hydrophilic radical polymerization nature polarity kind and a hydrophobic radical polymerization nature monomer substantially, and such microemulsion.

[0015]

[Means for Solving the Problem]Polymer composite of this invention includes an optical start polymerization product of microemulsion which has a nonporous double continuation structure substantially and has aqueous phase and an oil phase. said microemulsion -- the following -- (a) - the (e):(a) water 2 [about] - about 40 % of the weight;

(b) the radical copolymeric ethylene system unsaturation polarity kind 2 [about] - about 60 % of the weight;

(c) the radical copolymeric ethylene system unsaturation hydrophobic monomer 15 [about] - about 85 % of the weight;

(d). Do not carry out copolymerization to a polar kind of (1) ingredient (b), and a monomer of an ingredient (c). A nonionic surface active agent, a cationic surface active agent, anionic surface active agents, and these mixtures, (2).

Copolymerization can be carried out to a polar kind of an ingredient (b), and a monomer of an ingredient (c). An ethylene system unsaturation nonionic surface active agent, a cationic surface active agent, anionic surface active agents and these mixtures, the surface-active agent 5 [about] chosen from a group which comprises both (3), (1), and (2) - about 70 % of

the weight; and the (e) oleophilic photoinitiator 0.01 [about] - about 5 weight sections; It includes [however, the amount of photoinitiators of (e) is based on gross weight of the above (a), (b), (c), and (d) for weight % of the above (a), (b), (c), and (d) on the basis of gross weight of microemulsion, respectively]. Said both of polymerization products have a double phase of double continuation structure which is a nonporous solid substantially.

[0016]A unique double continuation polymer system of this invention is acquired as a result of carrying out the simultaneous polymerization of the radical pile affinity kind in both aqueous phase of microemulsion, and an organic phase. At the time of a simultaneous polymerization in each phase, aqueous phase and an organic phase live together in the state of the mutually united continuation domain. They are double continuity.

[0017]In this way, while a polymerization in aqueous phase brings about hydrophilic polymer which has hydrophilic bulk properties, a polymerization in an oil phase brings about a hydrophobic polymer which has hydrophobic bulk properties. Since a simultaneous polymerization takes place, polymer composite of nonporosity substantially which has both hydrophilic polymer and a hydrophobic polymer is obtained. There is that no one of polymer serves as a disperse phase substantially, it lives together as a domain where both of the polymer continued substantially, and a composite material obtained as a result serves as nonporosity and double continuity substantially. This polymer composite has two solid phases, and one hydrophilic polymer and a hydrophobic polymer of another side live together as a nonporous double continuation structure substantially.

[0018]Although not limited to a specific theory, polymer composite of this invention has both a hydrophobic continuous phase and a hydrophilic continuous phase as a gestalt formed when microemulsion is polymerized. A hydrophobic continuous phase is formed when a hydrophobic monomer polymerizes, and a hydrophilic continuous phase is formed when a hydrophilic monomer polymerizes. A microemulsion constituent produced by polymerizing shows the characteristic with both hydrophilic nature which followed continuous hydrophobicity, and can

perform neither of things for which a solvent of a hydrophobic polymer also dissolves a microemulsion constituent produced by a solvent of hydrophilic polymer polymerizing.

[0019]***** [that there are an independent hydrophobic polymer and hydrophilic polymer which are together put at the time of a polymerization so that mechanical concentration which can resist a solvation may be formed]. About whether copolymerization is carried out, some do not understand a hydrophobic monomer and a hydrophilic monomer at present so that a hydrophobic monomer and a hydrophilic monomer may form concentration of chemical share nature in a field which carried out copolymerization.

[0020]Even if a gestalt of polymer composite of this invention is a case where an exact gestalt cannot describe with a molecular level, one side of a phase is distributing and another side differs from a two phase form composite material which is continuation. A constituent of this invention is because bulk properties by the continuity of a hydrophobic polymer phase and bulk properties by the continuity of a hydrophilic polymer phase are compatible. "Double continuation structure" is a term for describing a gestalt of microemulsion after a polymerization with which the characteristic by a hydrophobic continuous phase and the characteristic by a hydrophilic continuous phase are compatible.

[0021]A method of this invention is also important for a gestalt of polymer composite obtained. A mixture remains as microemulsion stable at the time of a polymerization, and in order for polymer composite moreover obtained to show structure concentration nature, both of the monomers of a kind need to polymerize promptly. The quick and controllable polymerizing method which makes it possible to keep ["freezing" or] a gestalt of microemulsion stable, and to stop phase separation of microemulsion to the minimum, and to obtain nonporous polymer composite substantially in the case of a polymerization is a radical polymerization method which uses a photoinitiator and an electromagnetism radiant ray. Although it is possible as comparison to form nonporous polymer composite substantially under heat start radical polymerization conditions using a monomer illustrated by the US,5,238,992,B Description (Outubuddin) under a certain kind of conditions, There is a

limitation in the capability for a thermal initiation to be controllable. Since control of polymerization reaction speed is difficult, by the heat induction polymerizing method, there is a possibility that a gestalt of polymer composite obtained may change. Since this invention tends to control a direction which a gestalt of microemulsion in the case of a polymerization (microemulsion after a polymerization obtained if it lengthens) depends on the optical starting method compared with the heat starting method and can attain a gestalt of a request of polymer composite of this invention, photopolymerization method is used for it.

[0022] If the optical start polymerizing method is adopted as an unexpected thing, a nonporous composite material will be formed certainly substantially [request / of this invention]. In order for a Reason which photopolymerization method can trust dramatically to start a polymerization, it is not necessary to change temperature. photopolymerization method stops [that a polymerization is controllable (for example, a case where an electromagnetism radiant ray is irradiated -- as long as -- a polymerization takes place), and] phase separation of microemulsion at the time of photopolymerization to the minimum -- it comes out.

[0023] The US, 5,238,992, B Description will have indicated that a porosity polymer blend and a composite material are formed preferentially, if the heat start polymerizing method is used. This invention is not the heat start polymerizing method, and eliminates a porous blend and a composite material by providing polymer composite which was prepared with photopolymerization method and which has a nonporous double continuation structure substantially.

[0024] A term "it is nonporosity substantially" in this Description means that a stoma or open space in a composite material does not exist on a level which exceeds 0.1 micrometer in diameter. "It is nonporosity substantially", The US, 5,238,992, B Description and "Preparation and Characterization of Porous Polymers from Microemulsions" (ACS.) of Qutubuddin and others Chapter 5 of Symposium Series 384, It is clearly distinguished from porous structure in a micrometer level indicated to Polymer Association Structures, American Chemical Society, and 1989.

[0025]Aqueous phase is provided with the following.

Water.

At least one sort of radical copolymeric ethylene system unsaturation polarity kinds, for example, a monomer, and/or oligomer.

This aqueous phase if needed A refractoriness polarity oligomer additive agent, a radical polymerization nature photochemistry activation cross linking agent, One or more sorts of ingredients chosen from a group which comprises an auxiliary solvent, a water-soluble radical photopolymerization initiator, a water-soluble radical thermal initiator, and (it is (like an additive agent chosen from a group which comprises an electrolyte, a color, and a substance [activity / in drugs])) a water-soluble functional additive agent can be included further.

[0026]A term "polarity" in this Description means a kind in which a measurable dipole moment is shown, and a term "oligomer" means the Polymer Division kind which has a repeating unit to about 2000 pieces by two or more pieces and the maximum.

[0027]An organic phase contains an ethylene system unsaturation hydrophobic monomer of at least one sort of radical polymerization nature, an ethylene system unsaturation polar monomer of radical polymerization nature, and an oil-soluble radical photopolymerization initiator. An oil-soluble cross linking agent which this organic phase can contribute to the bulk properties of a refractoriness polarity oligomer additive agent and a constituent obtained if needed, One or more sorts of ingredients chosen from a group which comprises an oil-soluble chain transfer agent, an oil-soluble radical thermal initiator, and (as [chose / out of a group which comprises a plasticizer, a color, a substance / activity / in drugs /, and a tackifier]) an oil-soluble functional additive agent can be included further.

[0028]The third basic component of microemulsion is a surface-active agent of nonionic or ionicity (an example, anionic, or cationicity), and compatibility that can be anionic or nonionic preferably. If suitable, it will dissolve in neither an organic phase nor aqueous phase, but an additive agent and a bulking agent (for example, a web, scrim or silica, activity carbon black, or a fibrous filler) by which it is arranged inside

the last polymer composite which has a nonporous double continuation structure substantially and in which it deals may be made to contain.

[0029]Even if it mixes an ingredient which composes aqueous phase, an organic phase, and a surface-active agent in which order, transparent microemulsion forms spontaneously.

Subsequently, carry out the cast of the microemulsion into a suitable metallic mold, may irradiate with an electromagnetism radiant ray, may carry out a radical polymerization promptly, and. Apply microemulsion on a base material, on the base material, may irradiate with an electromagnetism radiant ray, may carry out a radical polymerization promptly, and, Or the cast of the microemulsion may be carried out so that a sheet or reinforcement of mesh state, for example, scrim etc., may be included, and it may irradiate with an electromagnetism radiant ray, and a radical polymerization may be carried out promptly. in these various methods -- "quick" -- it means that a polymerization takes place so that a nonporous double continuation structure may be substantially acquired in polymer composite, without a gestalt of microemulsion changing substantially in the case of a polymerization.

[0030]Preferably, electromagnetism radiant rays are ultraviolet rays which activate a photoinitiator in microemulsion and enable a monomer in microemulsion, and/or a simultaneous polymerization of oligomer. Obtained polymer composite which has a nonporous double continuation structure substantially can be made into adhesiveness and print resistance by operation of a used hydrophobic monomer. This whole system characteristic can be adjusted with an ingredient in both aqueous phase and an organic phase.

[0031]A nonporous double continuation structure can be inspected with a scanning electron microscope substantially [polymer composite / of this invention]. In a micron and a submicron level, as it is in a scanning electron microscope photograph of drawing 4, for example, it turns out that there is not a stoma or open space into polymer composite of this invention.

[0032]The feature of this invention is at a point that the bulk properties of hydrophilic polymer (it polymerizes in aqueous phase of microemulsion) and the bulk properties of a hydrophobic

polymer (it polymerizes in an oil phase of microemulsion) live together. Another feature of this invention has a composite material of this invention in improving the conventional hydrophobic polymer with the bulk properties of hydrophilic polymer, and a point which makes the reverse possible.

[0033]An advantage of this invention is that neither of the phases of polymer composite is the disperse phases in which continuity has broken off in a composite material. Another advantage of this invention is that the quick optical start polymerizing method brings about nonporous polymer composite substantially.

[0034]I. Before an aqueous-phase polymerization start, aqueous phase of microemulsion contains a water-soluble additive agent a water-soluble initiator and if needed water, an ethylene system unsaturation polarity kind of radical (**)
polymerization nature, and if needed.

I.a. microemulsion of the Mizumoto invention -- a gross weight standard of microemulsion -- about 2- about 40 % of the weight -- desirable -- about 5- about 30 % of the weight -- and -- most -- desirable -- about 6- about 20% of the weight of water is included. Preferably, microemulsion contains deionized water.

[0035]I.b. aqueous phase of an ethylene system unsaturation polarity Tanemoto invention of radical (**)
polymerization nature -- water -- in addition, include an ethylene system unsaturation polarity kind of radical polymerization nature. Polar monomers other than a monomer such whose a polar kind is insolubility substantially in an oil phase, and an oil insolubility monomer. It is chosen from (namely, a monomer which are water solubility and oil solubility), and a group which comprises polar oligomer (namely, oligomer which is hydrophilic oligomer or water solubility, and oil solubility which are insolubility substantially in an oil phase). Such a monomer is chosen from a group which comprises polar monomers (namely, water solubility and an oil-soluble monomer) other than a polar monomer which is insolubility substantially, and an oil insolubility monomer in an oil phase.

[0036]microemulsion -- character of a request of polymer composite -- a gross weight standard of microemulsion -- about 2- about 60 % of the weight -- desirable -- about 5- about 50 % of the weight -- and -- most -- desirable -- about 8- about 40%

of the weight of a required polar kind is included cumulatively. I.b.i. it is insolubility substantially in a polar ethylene system unsaturation radical (**) polymerization nature oligomer oil phase. Or useful polar ethylene system unsaturation radical (**) polymerization nature oligomer which is water solubility and oil solubility, Although not necessarily restricted, polyethylene oxide acrylate, polyethylene oxide diacrylate, What was chosen from a group which comprises polyethylene-glycol acrylate, polyethylene-glycol diacrylate, polyurethane acrylate, polyurethane diacrylate, N-vinyl-pyrrolidone macromere, and those mixtures is included. Polyethylene oxide acrylate and diacrylate are preferred. The most desirable oligomer contains polyethylene oxide acrylate from a Reason of acquisition ease and combination ease. Useful oligomer for the optimal physical properties (for example, absorptivity, nonporosity nature, intensity) of polymer composite which usually has a nonporous double continuation structure substantially, about 100 - about 100,000 -- desirable -- about 100 - about 60,000 -- and it has about 100 - about 5000 number average molecular weight most preferably.

[0037]I.b.ii. a polar monomer of the first type of an ethylene system unsaturation polar monomer of the radical (**) polymerization nature of oil insolubility is an ethylene system unsaturation polar monomer of water-soluble radical (**) polymerization nature which is insolubility substantially in an oil phase substantially. Both "it being oil insolubility (it is insolubility in an oil phase) substantially" and "water solubility." It means that a monomer has less than about 0.5% of the weight of solubility in an oil phase, and a partition ratio in a predetermined temperature (preferably about 25 ** - 35 **) of concentration in an oil phase to concentration in aqueous phase shows less than about 0.005. Such a monomer may be nonionic, for example, acrylamide, or may be ionicity. A mixture of non-ion and an ionicity monomer may be used. An ionicity monomer which suits these standards, Although not necessarily restricted, sodium styrenesulfonate, acrylic acid potassium, Sodium acrylate, sodium methacrylate, acrylic acid ammonium, Sodium 2-acrylamide 2-methylpropanesulfonate, 4,4,9-trimethyl 4-azonia 7-oxa ****- 9-****- 1-sulfonate, A

N,N-dimethyl- N-(beta-metacryloxy ethyl) ammonium propionate betaine, What was chosen from a group which comprises ethylene system unsaturated monomers of other dipolar ion nature which has trimethylamine methacrylamide, 1,1-dimethyl-1-(2,3-dihydroxypropyl) amine methacrylamide, and the required requirements for solubility, those mixtures, etc. is included. A desirable polar monomer of oil insolubility from a Reason of the ease of combination, and the physical properties of a request when it polymerizes. What was chosen from a group which comprises acrylamide, sodium styrenesulfonate, sodium acrylate, 2-acrylamido-2-methyl-propane-sulfonic-acid sodium, sodium methacrylate, and those mixtures is included.

[0038]I. Many polar monomers known by this ethylene system unsaturation polar monomer industry of radical (**) polymerization nature other than b.iiiI.b.ii show a certain amount of solubility to both water and an oil. They have about 0.5% or more of solubility in an oil phase, and a partition ratio in a predetermined temperature (preferably about 25 ** - 30 **) of concentration in an oil phase to concentration in aqueous phase shows about 0.005 or more. A radical (**) polymerization nature monomer of a useful polar ethylene system unsaturation which can be distributed between an oil phase of microemulsion of this invention and aqueous phase, Although not necessarily restricted, N-vinyl pyrrolidone, N-vinylcaprolactam, (METO) Acrylic acid, hydroxyethyl (METO) acrylate, itaconic acid, What was chosen from a group which comprises styrene-sulfonic-acid, N-substitution acrylamide, N,N-2 substitution acrylamide, N, and N-dimethylaminoethyl methacrylate, 2-acrylamido-2-methyl propane sulfonic acid, and those mixtures is included. A monomer in which desirable polar distribution is possible Acrylic acid (METO), N-vinyl pyrrolidone, What was chosen from a group which comprises N-vinylcaprolactam, N, and N-dimethylaminoethyl methacrylate, N,N-dimethylacrylamide, styrene sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, and those mixtures is included. A monomer in which the most desirable polar distribution is possible from a Reason of desirable character like physical strength which they can give to polymer composite. What was chosen from a group which comprises acrylic acid, N-vinyl pyrrolidone, N-vinylcaprolactam, N,N-dimethylacrylamide, and those mixtures is included.

[0039]I.c. water-soluble initiator aqueous phase may contain further a water-soluble radical polymerization initiator chosen from a group which comprises a mixture of a photoinitiator, and a photoinitiator and a thermal initiator if needed.

I.c.i. a water-soluble photoinitiator useful to water-soluble photoinitiator this invention -- a radiant ray (usually) When exposed to ultraviolet rays, it is a photoinitiator which generates a free radical, and it acts as an initiator for a polymerization (**) of the following polymerization (**) nature surface-active agent, a hydrophilic monomer, an oleophilic monomer, polymerization (**) nature oligomer, and when it exists. Benzophenone replaced by an ion portion, a hydrophilic portion, or its both although a useful water-soluble photoinitiator was not restricted; An ion portion, A thioxan ton replaced by a hydrophilic portion or its both and 4-substituent contain what was chosen from a group which comprises 4-substitution-(2-hydroxy-2-propyl) phenyl ketone which is ion or a hydrophilic portion. Although such ion or a hydrophilic portion is not necessarily restricted, it contains a portion chosen from a group which comprises hydroxyl, a carboxyl group, and a basis of carboxylate. Although water-soluble useful benzophenone is not necessarily restricted, it contains what was chosen from a group which comprises a 4-trimethyl aminomethyl benzophenone hydrochloride and benzophenone 4-sodium methanesulfonate. Although a water-soluble useful thioxan ton is not necessarily restricted, 3-(2-hydroxy-3-trimethyl aminopropoxy) thioxan ton hydrochloride, What was chosen from a group which comprises 3-(3-trimethyl aminopropoxy) thioxan ton hydrochloride, thioxan ton 3-(2-ethoxysulfonic acid) sodium salt, and thioxan ton 3-(3-propoxysulfonic acid) sodium salt is included. Although water-soluble useful phenyl ketone is not necessarily restricted, ketone (4(2-hydroxy-2-propyl)-diethylene-glycol phenyl), (2-hydroxy-2-propyl) What was chosen from ketone and a group which comprises those water soluble salt is included (phenyl-4-butane carboxylate). A desirable water-soluble photoinitiator is a 4-trimethyl aminomethyl benzophenone hydrochloride.

[0040]aqueous phase -- a standard [weight sections / all the

(**) / in microemulsion / heavy affinity kind 100] -- about 0.05- about 1 weight section, preferably, a photoinitiator of about 0.1 - about 1 weight section is included, when used.

I.c.ii. a water-soluble thermal initiator useful to water-soluble arbitrary thermal initiator this inventions, When it exists (**) and is exposed [a hydrophilic monomer, an oleophilic monomer, polymerization (**) nature oligomer, and] to heat which starts a polymerization (**) of a polymerization nature surface-active agent, it is an initiator which generates a free radical, and it indicates in detail to the following. These thermal initiators are used only as assistance of a photoinitiator, when a perfect polymerization of a monomer has concern. Although a water-soluble suitable thermal initiator is not necessarily restricted, potassium persulfate, Ammonium persulfate, sodium persulfate, and those mixtures; A oxidation reduction initiator, For example, resultant; and 4,4'-azobis (the soluble salts 4-cyanopentanone acid and its) of a reducing agent which is chosen from a group which comprises sodium metabisulfite and sodium bisulfite, and the above-mentioned persulfate What was chosen from a group which comprises (for example, sodium salt and potassium salt) is included. A water-soluble desirable thermal initiator is ammonium persulfate. Preferably, almost all water-soluble thermal initiator is used at temperature of about 50 ** - about 70 **, and, on the other hand, a oxidation reduction type initiator is used at temperature of about 30 ** - about 50 **. a time of being used -- a water-soluble thermal initiator -- a standard [weight section / in microemulsion / heavy (**) affinity kind 100] -- about 0.05- about 0.1 - about 1 weight section are included preferably about 1 weight section.

[0041]I.d. water-soluble additive agent aqueous phase may contain water-soluble various additive agents further if needed, in order to manufacture polymer composite which has specific character and/or appearance. Each additive agent is chosen so that a desired final product may be manufactured. For example, supposing a conductive polymer is desired, an electrolyte will be added and it will get. Supposing coloring polymer is desired, a color will be added and it will get. Although an example of a useful additive agent is not necessarily restricted, a water-soluble cross linking agent. What was chosen from (for

example, methylenebis acrylamide), a pH adjuster, an electrolyte, a color, paints, a compound [activity / in drugs], and a group that comprises an activity compound, an auxiliary solvent, non-copolymeric polarity oligomer, those mixtures, etc. physiologically is included. Although not necessarily restricted, when it was desirable for polymer composite to be conductivity as for especially an electrolyte containing what chosen from a group which comprises potassium chloride, a lithium chloride, sodium chloride, and those mixtures, a useful thing became clear with various compounds of this invention. On the basis of all the 100 weight sections of aqueous phase, an electrolyte to about 5 weight sections may be contained at the maximum, and about 0.5 weight sections - about 3 weight sections are contained preferably.

[0042]Although non-copolymeric polar oligomer useful as an additive agent is not necessarily restricted, it contains what was chosen from a group which comprises poly(N-vinylpyrrolidone), a polyethylene glycol, poly(oxyethylene) alcohol, poly (ethyleneimine), and those mixtures. Such oligomer is added so that the bulk properties of obtained polymer composite may be affected, for example, so that hydrophilic nature may be given to this material. Fatty alcohol which has about 1 - a carbon atom of eight abbreviation although the usual auxiliary solvent is not necessarily restricted. (for example, glycerin) and polyether (for example, butyl cellosolve (trademark).) It is butylcarbitol (trademark), hexyl cellosolve (trademark), and hexylcarbitol (trademark), and what was chosen from marketing and a group which comprises those mixtures is altogether included from Union Carbide.

[0043]A thing which is added to aqueous phase and which show solubility with all the water-soluble organic additive agents specific in an organic phase of microemulsion intrinsically will be understood easily. Each additive agent has the original partition ratio between aqueous phase and an organic phase. For this reason, as long as there are no directions in particular, the above-mentioned constituent of aqueous phase exists also in an organic phase, and will affect that character. It is unnecessary to an understanding and implementation of this invention, and to change a fixed quantity of all the specific partition ratios. [an additive agent indicated so far]

II. An oil phase term "organic phase", a "oil phase", and a "lipophilic phase" are used for a mutual compatible target in this Description. Before a polymerization start, an oil phase of microemulsion contains a reactant oleophilic additive agent a hydrophobic radical (**) polymerization nature monomer, a radical (**) polymerization nature polar monomer, an oil-soluble initiator, and if needed.

[0044]II.a. in a lipophilic phase of microemulsion of hydrophobic radical (**) polymerization nature monomer this invention, a useful ethylene system unsaturated monomer of hydrophobic radical polymerization nature, Although not necessarily restricted, what was chosen from a group which comprises ester derived from about C₁ of acrylic acid or methacrylic acid - abbreviation C₁₈ alkyl ester, i.e., acrylic acid, or methacrylic acid, and about C₁ - abbreviation C₁₈ alcohol is included. Desirable acrylic (METO) acrylate Isononyl acrylate, What was chosen from a group which comprises isooctyl acrylate, 2-ethylhexyl acrylate, ethyl acrylate, n-butyl acrylate, decyl acrylate, dodecylacrylate, isobornyl acrylate, methyl methacrylate, and those mixtures is included. The most desirable alkyl acrylate monomer is chosen from a group which comprises ethyl acrylate, n-butyl acrylate, isooctyl acrylate, isobornyl acrylate, methyl methacrylate, and those mixtures.

[0045]An organic phase contains further the above-mentioned alkyl acrylate monomer and copolymerizable radical polymerization nature ethylene system unsaturation comonomer if needed, in order to change glass transition temperature (T_g) of polymer composite obtained. Desirable comonomer Styrene, acrylonitrile, and vinyl ester. Comonomer is chosen by character of a request of double continuation polymer of the last solid including what was chosen from a group which comprises (for example, vinyl acetate, vinyl propionate, vinyl neo pentanoate, etc.). Double continuation microemulsion of this invention and in order to give sufficient intensity and cohesiveness for polymer composite produced by being manufactured, a gross weight standard of microemulsion -- about 15- about 85 % of the weight -- desirable -- about 25- about 75 % of the weight -- and -- most -- desirable -- about 30- about 65% of the weight of a hydrophobic monomer is included.

Presentation percent of each constituent in microemulsion will

be determined by person skilled in the art on the basis of character of a request of a copolymer, as stated above. It explains further what selection of a ratio of a constituent is made, and the following working example and drawing 1 - a phase diagram of three illustrate it.

[0046]II.b. a radical (**) polymerization nature polar monomer -- as mentioned above, in order that an organic substance may distribute between the organic phase/aqueous phase of microemulsion, an organic phase of microemulsion, Probably, a part of radical polymerization nature polar monomer indicated by above-mentioned I.b.ii. and I.b.iii. is included when used. Each monomer indicated in it shows the original partition ratio, and the listing is not required because of an understanding of this invention, and implementation.

II.c. an oil-soluble initiator oil phase contains an oil-soluble radical photopolymerization initiator (photoinitiator), and contains a thermal initiator further if needed.

[0047]II.c.i. oil-soluble photoinitiator this invention -- a useful oil-soluble photoinitiator -- a radiant ray (usually) When exposed to ultraviolet rays, a free radical is generated, and it acts as an initiator for a polymerization (**) of a polymerization nature surface-active agent, a hydrophilic monomer and/or oligomer, an oleophilic monomer, and when it exists (**). Although a useful photoinitiator is not necessarily restricted, it is a mixture of one Michler's ketone and benzyl, or benzophenone, What was chosen as 2 US, 4,289,844, B which is about 1:4 weight ratio preferably from a photoinitiator system of a coumarin base of a description and a group which comprises preferably a system which uses 3 dimethoxyphenylacetophenone and/or a diethoxyacetophenone as a base is included. An oil-soluble photoinitiator is contained in microemulsion as a part of organic phase at first. A free radical by which it was generated at the time of an exposure performs a polymerization (**) of a monomer, and (**) a polymerization (**) of a polymerization nature surface-active agent by both water and an organic phase. An organic phase contains about 0.01 - an oil-soluble photoinitiator of about 5 weight sections on the basis of all the (**) heavy affinity kind 100 weight section of microemulsion.

[0048]II.c.ii. in manufacture of double continuation polymer of this invention, arbitrary oil-soluble thermal initiator oil-soluble thermal initiators may be used for the above after a photopolymerization process like a description if needed, in order to complete a polymerization reaction. An oil-soluble thermal initiator useful to this invention is an initiator which generates a free radical, when exposed to heat, and it starts a polymerization (**) of a polymerization nature surface-active agent, a hydrophilic monomer, oligomer, an oleophilic monomer, and when it exists, and it explains it to the following in detail. Although a suitable oil-soluble thermal initiator is not necessarily restricted, An azo compound like Vazo 64 (trademark) (2,2'-azobis (isobutyronitrile)) and Vazo 52 (trademark) (2,2'-azobis (2,4-dimethylpentanenitril)) (available [from duPont] in both); Benzoyl peroxide. And what is chosen from a group which comprises peroxides like lauroyl peroxide and those mixtures is included. A desirable oil-soluble thermal initiator is 2,2'-azobis (isobutyronitrile).

[0049]an organic phase -- a standard [weight section / of a polymerization (**) nature compound in microemulsion / gross weight 100] -- about 0 - about 5 weight sections -- usually -- being alike -- about 0.05- about 5 weight sections, preferably, about 0.1 - an oil-soluble thermal initiator of about 5 weight sections are included, supposing it is used. II.d. arbitrary reactant oleophilic additive agent organic phases may contain further one or more sorts of further radical reactivity constituents if needed, and although they are not necessarily restricted, they contain what was chosen from a group which comprises an oil-soluble cross linking agent, chain transfer agents, and those mixtures. Although an example of a useful cross linking agent is not necessarily restricted, divinylbenzene; 1,4-butanediol diacrylate, What was chosen from a group which comprises abbreviation C₄-abbreviation C₈ alkyl diacrylate; which is chosen from a group which comprises 1,6-hexanediol diacrylate, 1, and 8-octanediol diacrylate, and those mixtures is included. A desirable cross linking agent is 1,6-hexanediol diacrylate. Supposing a cross linking agent is added, it will change, last physical properties, for example, condensation intensity, of polymer. An organic phase is further

included if needed, supposing it uses about 0.1 - a cross linking agent of 75 % of the weight of abbreviation for about 0 - about 75 weight sections or more than it, and usual on the basis of all the oil phase 100 weight section. Quantity of a cross linking agent used determines the physical properties of polymer, for example, insolubility to inside of a solvent, an elastic modulus, and internal strength. In such a use, an organic phase usually contains a cross linking agent of about 5 - about 75 weight sections on the basis of oil phase 100 weight section. In order that a person skilled in the art may acquire desired physical properties, quantity of a suitable cross linking agent can be determined, and he will understand that there is no maximum on actual of a cross linking agent by which such a person skilled in the art is used in a compound of this invention and in which it deals.

[0050]An organic phase contains a chain transfer agent further if needed. Although an example of a useful chain transfer agent is not necessarily restricted, it contains what was chosen from a group which comprises carbon tetrabromide, alcohol, mercaptan, and those mixtures. When it exists, a desirable chain transfer agent is isooctylthioglycolate. supposing an oil phase is used -- a standard [weight sections / all the / oil phase 100] -- the maximum -- a chain transfer agent to about 0.5 weight sections -- usually -- being alike -- about 0.01- a chain transfer agent of about 0.05 - about 0.2 weight sections may be included further preferably about 0.5 weight sections.

II.e. arbitrary refractoriness oleophilic additive agent oil phases contain further one or more sorts of refractoriness oil-soluble additive agents if needed. Various refractoriness oil-soluble additive agents may be contained in microemulsion. Such materials are added so that it may have last physical properties or appearance with a specific polymer system and may be manufactured. Although an example of such arbitrary oleophilic additive agents is not necessarily restricted, it contains what was chosen as this industry from a group which comprises a plasticizer like one sort of phthalic ester known well. supposing an oil phase is used -- a standard [weight section / oil phase 100] -- about 0 - about 20 weight sections -- usually -- being alike -- about 5- a plasticizer of about 8 - about 15 weight sections is included preferably about 20

weight sections.

[0051] In order to prepare surface-active agent microemulsion, it argues about non-ion and an ion (anion and cation) surface-active agent which are used for this invention below. A surface-active agent may be [which exist in microemulsion / a monomer and copolymeric], or may be non-copolymeric. As for a surface-active agent, it is preferred that it is copolymeric so that polymer composite obtained may seldom become hypersensitivity in water. When tolerance to water is unnecessary, a non-copolymeric surface-active agent is preferred from a Reason for the cost low generally.

1. A nonionic surface active agent nonionic surface active agent is usually a condensation product of alkylene oxide which is organic aliphatic series or an alkyl aromatic hydrophobic compound, and hydrophilic nature, for example, ethylene oxide. it has carboxy, hydroxy ** amide, or an amino group in which the free water matter exists -- all hydrophobic compounds are almost condensed with ethylene oxide, and a nonionic surface active agent can be formed. It is adjusted and deals in the length of ethylene oxide chains of a condensation product so that desired hydrophobicity and balance (hydrophilic-hydrophobic balance, i.e., HLB) of a hydrophilic component may be attained. HLB of a surface-active agent -- size of the hydrophilic nature (***** or polarity) of a surface-active agent, and a hydrophobic (***** or nonpolarity) basis, and balance of strength -- expressing . HLB of a nonionic surface active agent useful to this invention in order to prepare microemulsion -- about 6 - about 19 -- desirable -- about 9 - about 18 -- and it is about 10 - about 16 most preferably. A useful nonionic surface active agent contains what was chosen from a group which comprises copolymeric nonionic surface active agents and those mixtures of a nonionic surface active agent of un-(**) polymerizing nature, and an ethylene system unsaturation.

[0052] 1.a. A non-copolymeric nonionic surface active agent, especially a nonionic surface active agent of useful refractoriness, So that HLB specified above may be attained, although not necessarily restricted, Fatty alcohol containing high-class fatty alcohol of straight chain shape or the shape of a branched chain -, for example, about 8, and a carbon atom of 20 abbreviation, and about 3 - 100 mol of abbreviation, What

is chosen from a group which comprises preferably a condensation product of about 5 - 40 mol of abbreviation which about 5 - ethylene oxide of 20 mol of abbreviation condensed most preferably is included. Examples of an ethoxylation fatty alcohol surface-active agent of such non-ion are Tergitol(trademark)15-S series of Union Carbide, and a Brij (trademark) surface-active agent of ICI. A Tergitol(trademark)15-S surface-active agent contains C₁₁-C₁₅ secondary-alcohol polyethylene glycol ether. Brij(trademark)58 surface-active agent is polyoxyethylene (20) Sept Iles ether, and Brij(trademark)76 surface-active agent is polyoxyethylene (10) stearyl ether. Other suitable refractoriness nonionic surface active agents so that HLB specified above may be attained, although not necessarily restricted, 1 mol of alkylphenol containing about 6-12 carbon atoms of straight chain shape or the shape of a branched chain and a thing which was preferably chosen [about 5 - 40 mol of abbreviation] from a group which comprises about 5 - a polyethylene oxide condensate with 20 mol of abbreviation most preferably as for the ethylene oxide 3 [about] - 100 mol of abbreviation are included. An example of a refractory nonionic surface active agent is Igepal(trademark) CO and CA series of Rhone-Poulenc. An Igepal(trademark) CO surface-active agent contains nonylphenoxypoly(ethyleneoxy)ethanol. An Igepal(trademark) CA surface-active agent contains octylphenoxypoly(ethyleneoxy)ethanol.

[0053]Another group of an usable refractoriness nonionic surface active agent, Although not necessarily restricted, what was chosen from about 6 - about 19, and a group that comprises preferably block copolymer of about 9 - about 18, ethylene oxide that has about 10 - about 16 HLB value most preferably and propylene oxide, or butylene oxide is included. Examples of such a non-ion block copolymer surface-active agent are Pluronic (trademark) of BASF, and a surface-active agent of Tetronic (trademark) series. A Pluronic (trademark) surface-active agent contains ethylene oxide propylene oxide block copolymer. A Tetronic (trademark) surface-active agent contains ethylene oxide propylene oxide block copolymer. being the further -- others -- a refractoriness nonionic surface active agent satisfied, although not necessarily restricted -- about 6 -

about 19 -- desirable -- about 9 - about 18 -- and it has about 10 - about 16 HLB most preferably. What was chosen from a group which comprises a sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, and polyoxyethylene stearate is included. Examples of such a fatty-acid-ester nonionic surface active agent are Span (trademark) of ICI, Tween (trademark), and a Myrj (trademark) surface-active agent. A Span (trademark) surface-active agent contains C₁₂-C₁₈ sorbitan monoester. A Tween (trademark) surface-active agent contains poly (ethylene oxide) C₁₂-C₁₈ sorbitan monoester. A Myrj (trademark) surface-active agent contains polyethylene oxide stearate. [0054]

1.b. A suitable nonionic surface active agent for making it contain in microemulsion of ethylene system unsaturation copolymeric nonionic surface active agent this invention is an ethylene system unsaturation copolymeric nonionic surface active agent, Although not necessarily restricted, it is general formula $R-O-(R'O)_m-(EO)_{(n-1)}-CH_2CH_2OH$ (among a formula). R (about -- about [C₂-] -- C₁₈ alkenyl, AKURIRIRU, and AKURIRIRU (about C₁-about C₁₀) alkyl.) Methacrylyl, methacrylyl (about C₁-about C₁₀) alkyl, It is chosen from a group which comprises vinylphenyl and vinylphenylene (about C₁-about C₆) alkyl, and; R'O Two or more carbon atoms, It is chosen from a group which comprises an alkyleneoxy group of bivalence derived from an epoxy compound which has three pieces or four carbon atoms preferably, For example, propylene oxide, It is chosen from a group which comprises those mixtures, such as butylene oxide, and; E is ethylene of bivalence, ;m expresses about 5 - about 100 integer, ;n expresses about 5 - about 100 integer, and ratios of ;m to n are about 20:1 - abbreviation 1:20. What was chosen from a group which comprises an applicable thing is included. If a ratio of m and n is changed, HLB of a polymerization nature surface-active agent will change. HLB required for a nonionic surface active agent of this invention is about 6 - about 19, and is about 9 - about 18 preferably, and is about 10 - about 16 most preferably. An example of such a copolymeric nonionic surface active agent is an alkylene polyalkoxyethanol surface-active agent, and it is available with trade name Mazon BSN(trademark)185 from PPG Industries, and 186 and 187 in it. A Mazon BSN (trademark) surface-active agent contains alkylene

polyalkoxyethanol.

[0055]2. An anionic surface active agent anionic surface active agent, Usually, a hydrophobic part chosen from a group which comprises alkyl (about C₆-about C₂₀), alkyl aryl, and an alkenyl group, And sulfate, sulfonate, phosphate, polyoxyethylene sulfate, An anion group chosen from a group which comprises polyoxyethylene sulfonate, polyoxyethylene phosphate and alkali metal salt of such an anion group, ammonium salt, and the third class amino salt is included. As a hydrophobic part. (About C₂-about C₁₈) In this invention a specific ethylene system unsaturation copolymeric surface-active agent containing an anion group of alkenyl polyoxypropylene or (about C₂-about C₁₈) alkenyl polyoxy butylene, and polyoxyethylene sulfate. It is useful although microemulsion is manufactured. Further useful anionic surface active agent is described below to this invention.

[0056]2. a refractoriness anionic surface active agent which can be used in a. refractoriness anionic surface active agent this invention, Although not necessarily restricted, alkyl (about C₆-about C₂₀), alkyl aryl sulfate, or sulfonate, For example, Sodium lauryl sulfate (as Polystep(trademark) B-3 from Stepan Co.) Marketing and sodium dodecylbenzenesulfonate (it markets as Siponate(trademark) DS-10 from Rhone-Poulenc); They are polyoxyethylene (about C₆-about C₂₀) alkyl or alkylphenol ether sulfate, An ethylene oxide repeating unit in a surface-active agent is less than about 30 units, What is preferably less than about 20 units, and is most preferably less than about 15 units, For example, Polystep of marketing from StepanCo. (Trademark) B-1, Ailpal(trademark) EP110 of Rhone-Poulenc, and 115; They are alkyl (about C₆-about C₂₀) of phosphoric acid or alkyl phenoxy poly(ethyleneoxy) ethylmonoester, diester, and its salt, An ethylene oxide repeating unit in a surface-active agent contains what was chosen from a group which comprises a thing which is less than about 30 units, is preferably less than about 20 units, and is most preferably less than about 15 units, for example, Gafac(trademark) PE-510 of GAF, and Gafac(trademark) RE-610.

[0057]

2.b. A suitable anionic surface active agent for making it contain in microemulsion of ethylene system unsaturation

copolymeric anionic surface active agent this invention is formula $R-O-(R'O)_m-(EO)_{n-1}-CH_2CH_2X$, although not necessarily restricted. the inside of [type, and R (about -- about [C₂-] -- C₁₈ alkenyl --) [AKURIRIRU and] AKURIRIRU (about C₁-about C₁₀) alkyl, methacrylyl, It is chosen from a group which comprises methacrylyl (about C₁-about C₁₀) alkyl, vinylphenyl, and vinylphenylene (about C₁-about C₆) alkyl, and;R'O Two or more carbon atoms, An alkyleneoxy group of bivalence derived from an epoxy compound which has three pieces or four carbon atoms preferably, For example, it is chosen from a group which comprises mixtures of such an alkyleneoxy group, such as propylene oxide and butylene oxide, and;E is ethylene of bivalence,;m expresses about 5 - about 100 integer,;n expresses about 5 - about 100 integer, and ratios of;m to n are about 20:1 - abbreviation 1:20. What was chosen from a group which comprises an ethylene system unsaturation copolymeric surface-active agent of] is included. If a ratio of m and n is changed, HLB of a polymerization nature surface-active agent will change. HLB required for an anion copolymeric surface-active agent of this invention is about 3 - about 16 except for X-basis. X is the anion group chosen from a group which comprises alkali metal salt, ammonium salt, or the third class amino salt of sulfonate, sulfate, phosphate, and such an anion group. An example of such a copolymeric anionic surface active agent is Mazon(trademark) SAM 211 of PPG Industries and Inc.

[0058]1. In cationic surface active agent this invention a useful cationic surface active agent, Although not necessarily restricted, what was chosen from a group which comprises quarternary ammonium salt in which a basis of a lower molecular weight of a basis of a higher molecular weight of at least one piece and two pieces, or three pieces combined with a common nitrogen atom, and formed a cation is included. Here, an anion made to balance electrically is chosen from a group which comprises halogenides (a bromide, a chloride, etc.), acetate, nit RITTO, and low-grade ARUKO sulfate (METOSURU Fet etc.). a substituent of the amount of Polymer Division is often a higher alkyl group from that on nitrogen -- about 10-, including about 20 carbon atoms, More, the substituent of low molecular weight can be low-grade alkyl, for example, methyl, or ethyl of a carbon

atom of about 1 - four abbreviation, and it may be replaced by hydroxy **, for example depending on the case. One or more substituents may also contain an aryl portion, and it may be replaced by aryl, for example, benzyl, and phenyl. about 1- it being low-grade alkyl, for example, methyl, or ethyl of about four carbon atoms, being replaced by low-grade polyalkoxy portion like a polyoxyethylene portion, and, including a hydroxy end group, A thing applicable to general formula- $R(CH_2CH_2O)_{(n-1)}CH_2CH_2OH$ (-R is an alkyl group of bivalence of C_{1-4} combined with nitrogen among a formula, and n expresses about 1 - about 15 integer.) is contained in a possible low-molecular-weight substituent. Independently, it is not combined with quaternary nitrogen through the above-mentioned low-grade alkyl, but 1 of such a low-grade polyalkoxy portion that has hydroxyl of an end, or two pieces may couple directly with quaternary nitrogen. An example of a quaternary ammonium halide surface-active agent useful to use by this invention, Although not necessarily restricted, it is methylbis(2-hydroxyethyl)****- ammonium chloride or oleyl ammonium chloride (respectively) from Akzo Chemical Inc. What was chosen from a group which comprises Ethoquad(trademark) C/12, O/12, and methylpolyoxyethylene (15) octadecyl ammonium chloride (Ethoquad(trademark) 18/25) is included.

[0059] Typical constituent concentration (% of the weight) in microemulsion of this invention is as in the following table 1.

[0060]

[Table 1]

マイクロエマルジョン	有用	好適	最好適
疎水性モノマー	15-85%	25-75%	30-65%
水	2-40%	5-50%	8-40%
極性種	2-60%	5-50%	8-40%
界面活性剤	5-70%	7-50%	9-35%

[0061] Each numerical value in Table 1 shows a rough value. These figures express weight % to gross weight of microemulsion. Concentration of each ingredient is selected so that the whole may be 100%.

[0062] Since microemulsion forms spontaneously a manufacturing

method of microemulsion of manufacturing method this invention of microemulsion, without needing most intense stirring, it is comparatively easy. However, it is desirable to dissolve an oil-soluble photoinitiator in a hydrophobic monomer beforehand, and to dissolve beforehand all the water-soluble additive agents, an oil insolubility ionicity monomer, or a water-soluble photoinitiator in water, and to form a solution. Subsequently, transparent and homogeneous microemulsion which does not carry out phase separation even if it mixes with a polar monomer, a surface-active agent, and other additive agents of all the and carries out aging of this hydrophobic monomer mixture and solution is manufactured. It is not necessary to use heat and almost all mixing processes are mostly carried out suitably at a room temperature (20-30 **).

[0063]The phase transition between the transparent microemulsion of a 1 phase system of this invention and the emulsion in which the two phase system became muddy is shown in drawing 1 - drawing 3. These are only illustration although these figures show the three phase figure about a hydrophilic pile affinity phase, a hydrophobic pile affinity phase, and the concentration of a surface-active agent (polymerization nature or non-polymerizable) about a certain specific microemulsion.

[0064]Drawing 1 is a phase diagram showing a microemulsion field transparent about the desirable constituent of this invention, and the emulsion field which became muddy. In this constituent, from PPG Industries, a surface-active agent is polymerization nature anionic surface active agent and Mazon (trademark) SAM211 marketed, and the heavy affinity phase of hydrophilic nature, It is a mixture which contains polyoxyethylene acrylate (PEOA), deionized water, and potassium chloride by the weight ratio 68:30:2, and a hydrophobic heavy affinity phase is a mixture which contains isobornyl acrylate and acrylic acid by the weight ratio 85:15. The slash field of drawing 1 shows the density range where the useful microemulsion by this invention was obtained.

[0065]Drawing 2 is a phase diagram showing a microemulsion field transparent about the desirable constituent of this invention, and the emulsion field which became muddy. The non-polymerizable nonionic surface active agent in which the surface-active agent is marketed from Union Carbide in this

constituent, Are Tergitol15(trademark)-S-12 and the heavy affinity phase of hydrophilic nature, It is a mixture which contains polyoxyethylene acrylate, deionized water, and potassium chloride by the weight ratio 68:30:2, and a hydrophobic heavy affinity phase is a mixture which contains isobornyl acrylate and acrylic acid by the weight ratio 85:15. The slash field of drawing 2 shows the density range where the useful microemulsion by this invention was obtained.

[0066]Drawing 3 is a phase diagram showing a microemulsion field transparent about the desirable constituent of this invention, and the emulsion field which became muddy. In this constituent, surface-active agents are a non-polymerizable cationic surface active agent, and Ethoquad (trademark) C/12, and the heavy affinity phase of hydrophilic nature, It is a mixture which contains polyoxyethylene acrylate, deionized water, and potassium chloride by the weight ratio 68:30:2, and a hydrophobic heavy affinity phase is a mixture which contains isobornyl acrylate and N-vinyl pyrrolidone by the weight ratio 85:15. The slash field of drawing 3 shows the density range where the useful microemulsion by this invention was obtained.

[0067]If microemulsion is obtained, a radical polymerization will be made to start and a polymerization will be made to cause by irradiating a person skilled in the art with an electromagnetism radiant ray by a well-known technique. After applying microemulsion on a flexible carrier web by one means of the daily use, such as roller coating, dip coating, knife coating, or extrusion coating, In an inert atmosphere (namely, atmosphere which does not contain oxygen), using a nitrogen atmosphere as everyone knows etc. polymerizes in the technical field concerned.

[0068]The plastic film which does not penetrate oxygen although ultraviolet rays are penetrated substantially, After combining microemulsion with the polyester film which has a silicone series remover on the surface which contacts microemulsion preferably, Microemulsion can also be polymerized in the air by using the fluorescence type ultraviolet ray lamp which emits the UV light of the wavelength range which the used photoinitiator absorbs, and irradiating with microemulsion through this film. Several kinds of lamps marketed can be used. A medium-voltage mercury-vapor lamp and a low-strength

fluorescent lamp are in these, and it has various kinds of emission spectra, respectively, and the luminescence maximum is shown among 280-400 nm. It is preferred to use the fluorescence black light of marketing which has 90% of luminescence in the range which is 300-400 nm for convenience, and has the maximum in about 351 nm.

[0069] Generally, the total exposure dose should be made about 200-700 mJ [cm^{-2}]. The maximum efficiency and speed of a polymerization are shown by the used expression of relations of the absorption feature of a photoactive compound, and the radiation property of an irradiation source. When the 2,2-dimethoxy-2-phenyl-acetophenone (known also as 2,2-dimethoxy-2-phenyl-1-phenylethanone and benzyl dimethyl ketal) which is a desirable photoinitiator is used, It is preferred that it is while not less than about 75% of radiant rays are 300-400 nm.

[0070] Although photopolymerization can also be carried out in an inert atmosphere, it can raise the admissibility for oxygen by making an oxidizability tin compound contain in a constituent as it writes in the US, 4,303,485, B Description. As one of the photopolymerization method, after average light intensity irradiates microemulsion with the electromagnetism radiant ray of 0.01-20 mW [cm^{-2}] at about 280-500 nm first in wavelength, There is a way wavelength irradiates with the electromagnetism radiant ray whose average light intensity is higher than 20 mW [cm^{-2}] at about 280-500 nm.

[0071] Desirable photopolymerization method is sufficient method of carrying out a time exposure and giving about 680 mJ [cm^{-2}] about microemulsion in about 351-nm electromagnetism radiant ray. In this case, about 10-minute Hazama's photopolymerization time is required. Even if it gives continuously by the requirements for manufacture, the amount of ultraviolet energies which irradiates with this microemulsion is batch-like, and may be given. Microemulsion may be polymerized under ambient conditions. Ambient air temperature, ambient pressure, and ambient humidity are permissible.

[0072] If a polymerization is completed, superfluous moisture may be removed with the evaporation method which uses a convection furnace and the source of infrared rays if needed.

The conductivity of polymer was measured by the measure resistance method of the four measuring method probe type of the examining method conductivity. Four metallic pins which kept the equal interval D (cm) were pressed against the polymer sample with the spring. The current of the intensity I (ampere) was sent through the outside pin. The amount V of voltage drops between inside probes (bolt) was measured. Resistivity is computed by a lower formula.

Resistivity (Ωcm) = $2\pi DV/I$ conductivity is computed by a lower formula.

Conductivity = $1 / \text{resistivity}$ Reference documents :. L. J. van der Pauw, Philips Res. Repts. 16 (1961) 187; J. Hornstra and L. J. van der Pauw, J. Electronics and Control 7 (1959) 169. [0073]The following cable addresses and trademarks are used on the cable address and the trademark book Descriptions.

Comp. ; comparative example DI water; -- deionized water IBOA; -- isobornyl acrylate IOA ; Isooctyl acrylate MMA ; methyl methacrylate AA; -- acrylic acid NVP ; N-vinyl pyrrolidone AcM ; Acrylamide KAA. ; Acrylic acid potassium MazonTMSAM. 211 ; P PG. Alkylene polyalkoxy sulfate surface-active agent KCl made from Industries ; Potassium chloride PEOA; poly (ethylene oxide) acrylate or poly (oxyethylene) acrylate M.W.;. [Molecular weight TergitolTM15-S-12;] Union. Ethoxylated fatty alcohol surface-active agent TexaponTM L100 made from Carbide ; Sodium-lauryl-sulfate surface-active agent SiponateTMDS10 made from Henkel ; Dodecylbenzenesulfonic acid made from Rhone-Poulenc. The ammonium alkylphenol made from alkyl poly(ethyleneoxy) ethyl phosphate surface-active agent PolystepTMB-1;Stepan Chemical made from sodium surface-active agent GafacTMRE610;GAF. The ammonium alkylphenoxy poly(ethyleneoxy)ethanol sulfate surface-active agent made from ethoxy rate sulfate surface-active agent AlipalTMEP110;Rhone-Poulenc [0074]

[Example]Although the following working example explains this invention further, these working example does not limit this invention. Unless it refuses in particular, all of these working example and the part in the Description remainder, percent, a ratio, etc. are based on weight.

One to working example 6 working example 1-6 carries out the microemulsion which has the aqueous phase (hydrophilic phase)

and oil phase (canal phase) of the polymerization nature manufactured with polymerization nature and a non-polymerizable anionic surface active agent example 1. [0075]The solution which contains 0.5 g of potassium chloride (KCl) in 7.5 g of deionized water in the jar of 1200 ml of working example was prepared at the room temperature. 9.4 g of acrylic acid (AA) and 22.2 g of poly (ethylene oxide) acrylate (PEOA) were added to this solution, and the hydrophilic phase was prepared. Subsequently, 48.0 g of isobornyl acrylate (IBOA) and MazonTMSAM 211 12.5-g surface-active agent were mixed to the hydrophilic phase, and transparent microemulsion was obtained. The microemulsion of two to working example 6 working example 2-6 was prepared like working example 1 except for having used the ingredient and quantity which were displayed on the following table 2 instead of the ingredient and quantity which were indicated in working example 1.

[0076]

[Table 2]

実施例	重量 %					
	1	2	3	4	5	6
IBOA	48.0	35.5	33.4	32.9	32.5	31.8
AA	9.4	6.1	---	5.8	5.7	5.5
NVP	---	---	16.5	---	---	---
PEOA***	22.2	27.8	22.7	26.4	26.0	24.8
脱イオン水	7.4	12.2	10.0	11.6	11.4	10.9
KCl	0.5	---	0.7	0.8	0.7	---
Mazon TM SAM211*	12.5					
Texapon TM L100*		18.4				
Siponate TM DS10*			16.7			
Polystep TM B-1*				22.5		
Alipal TM BP110*					23.7	
Gafac TM RB610*						27.0

[0077]* All percents are based on the gross weight of microemulsion.

* Before using the anionic surface active agent of *PolystepTM B-1 and AlipalTMEP110 for preparation of microemulsion, it dried within a 105 ** furnace for about 10 to 15 hours, and it made activity 100%. The anionic surface active agent of MazonTMSAM

211, Texapon™ L100, Siponate™DS10, and Gafac™RE610 was used as it was. Mazon™SAM 211 is a copolymeric anionic surface active agent. Texapon™ L100, Siponate™DS10, Polystep™ B-1, Alipal™EP110, and Gafac™RE610 are non-copolymeric anionic surface active agents.

* Number average molecular weight =750 of ** PEOA [0078]Seven to working example 14 working example 7-14 illustrates the process of the microemulsion which has the aqueous phase (hydrophilic phase) and oil phase (canal phase) of the polymerization nature manufactured with the copolymeric and non-copolymeric nonionic surface active agent. These microemulsion was prepared like working example 1 except for having used the ingredient and quantity which were displayed on the following table 3 instead of the ingredient and quantity which were indicated in working example 1.

[0079]

[Table 3]

実施例	重量 %							
	7	8	9	10	11	12	13	14
IBOA	47.1	46.1	47.4	42.6	44.8	39.4	44.1	47.4
AA	9.3	9.0	9.2	8.3	8.7	7.7	8.6	9.2
PEOA***	23.5	22.8	23.3	21.1	22.1	19.5	21.9	23.3
脱イオン水	5.8	5.7	5.8	5.3	5.5	4.9	5.5	5.8
KCl	0.5	0.5	---	0.5	0.5	0.4	0.5	0.5
BSN™ 186*	13.8							
Igepal™ CA630*		15.9						
Tergitol™ 15-S-12*			14.3					
Pluronic™ L64*				22.2				
Tetronic™ 1304*					18.4			
Tween™ 20*						19.2		
Myrj™ 52*							19.2	
Brij™ 58*								13.8

[0080]* All percents are based on the gross weight of microemulsion.

* * BSN™186 is a copolymeric nonionic surface active agent made from PPG Industries.

It was then used (that is, it does not dry before use).

The remaining nonionic surface active agents of Table 3 are

non-copolymeric nonionic surface active agents, and were used as it was also about these (that is, it does not dry before use).
 * Number average molecular weight =750 of ** PEOA [0081]Working example 15 and 16 working example 15 and 16 illustrate the process of the microemulsion which has the hydrophilic phase and canal phase of the polymerization nature manufactured with the non-copolymeric cationic surface active agent. Although these microemulsion was prepared like working example 1, it used the ingredient and quantity which used N-vinyl pyrrolidone (NVP) instead of and were moreover displayed on the following table 4. [acrylic acid]
 [0082]
 [Table 4]

実施例	重量 % *	
	15	16
IBOA	31.3	35.6
NVP	8.0	7.1
PEOA***	14.7	31.3
脱イオン水	15.3	3.6
KCl	---	0.7
Ethoquad™ C/12*	30.7	
Ethoquad™ 18/25*		21.7

[0083]* All percents are based on the gross weight of microemulsion.

* * cationic surface active agent was used as it was (that is, it does not dry before use).

* Number average molecular weight =750 of ** PEOA [0084]The following working example 17-25 explains the process of the polymer composite which has the double continuation structure by the polymerization of microemulsion.

The solution which contains 0.5-g KCl in 8.8 g of deionized water in the jar of 17200 ml of process working example of the polymer which has the double continuation structure by the polymerization of microemulsion was prepared at the room temperature. 9.4 g AA and 20.8-g PEOA were added to this solution, and the hydrophilic phase was made to form. Subsequently, 47.7 g IBOA, Mazon™SAM211 12.5 g surface-active agent, and a 0.3-g benzyl dimethyl ketal photoinitiator were mixed to this

hydrophilic phase, and transparent microemulsion was obtained to it. Then, this transparent microemulsion was poured in into the 5cmx15cmx2mm cell demarcated with the glass of the couple which has a release liner. Subsequently, the cell containing microemulsion was irradiated with the product [made by General Electric] F40BL type 40-W UV light which generates 1.9mJ from the place distant 6 cm for 20 minutes at the room temperature, and the polymerization was made to cause. After the polymerization, according to the four-point probe type measure resistance method, as shown in Table 5, the polymer solid showed conductivity, and it suggested that polymer composite had taken double continuation structure.

[0085]In working example 18-24, the ingredient indicated to Table 5 in accordance with the above-mentioned method was mixed, and microemulsion was prepared, and solid polymer was prepared from the microemulsion. Polymer of hydrophilic nature, the adhesiveness by hydrophobic double continuation polymer composite, and non cohesiveness was manufactured by this method. The comparative example 25 comparative example 25 illustrates the process of polymer which is not double continuation. Although the procedure of working example 17 was adopted, however since deionized water was excluded, microemulsion was not formed. The obtained polymer was non-conducting intrinsically, as shown in Table 5.

[0086]

[Table 5]

実施例	重量 % *								
	17	18	19	20	21	22	23	24	比較例25
IBOA	47.7	56.1			22.5		48.3	48.8	47.7
IOA			50.9	46.2	22.5				
MMA						45.2			
ベンジルジメチルケタール	0.3	0.5	0.5	0.5	0.3	0.8	0.5	0.5	0.3
脱イオン水	8.8	6.0	10.0	7.7	8.5	8.5	11.3	9.5	
KCl	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PEOA***	20.8	23.0		22.3	20.0	20.0			20.8
AA	9.4		12.4		9.0	9.0		11.5	9.4
NVP				7.8					
AcM								2.5	
KAA							13.3		
Mazon SAM™211	12.5	13.8	25.7	15.0	16.0	16.0	26.1	26.7	12.5
*導電率×10 ⁻⁷	22	170	263	197	12	5	10	112	0.06

[0087]* All percents are based on the gross weight of microemulsion.

* Number average molecular weight =750 of $\omega^{-1}\text{cm}^{-1}$ *** PEOA
 [0088]The gestalt of the polymer which might be followed by working example 17 and 24 was observed by scanning electron microscope SEM (Bedford, goods Amray 1810 microscope marketed from Amray of MA.). Freeze fracturing of the sample is carried out in liquid nitrogen, And weld slag coating of the golden-palladium was carried out for 4 minutes at 10 kV using the sputtering system (Agawam, goods Ultra-Spec 90 LVC sputtering system marketed from Energy Beam Sciences of MA.). Magnification was made into 3000 or more times.

[0089]Drawing 4 shows the SEM microphotograph of polymer of working example 17. Polymer of working example 17 is flexible non cohesiveness polymer which has a nonporous gestalt substantially. 0.1 micrometers or more in diameter a stoma or open space were not accepted at all, but polymer was nonporosity substantially. Drawing 5 shows the SEM microphotograph of polymer of working example 24. Polymer of working example 24 is non cohesiveness polymer without the pliability which has a nonporous gestalt substantially. 0.1 micrometers or more in diameter a stoma or open space were not accepted at all, but

polymer was nonporosity substantially.

[0090] Polymer of working example 24 was prepared by the heat induction polymerizing method by the method indicated in working example of the US, 5,238,992, B Description (Outubuddin) for comparison. This polymer composite was non cohesiveness polymer without the pliability in which the big bubble was confined inside. It filled up, so that open space could not be permitted in this polymer, and it was not nonporosity substantially.

[0091] Although this invention was explained in connection with a special embodiment, please understand that it can change further. The Claims in this Description include such all transformation to be accepted if it is a person skilled in the art as it is chemically as equivalent as what was indicated here.